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MECHANISM OF THE DECOMPOSITION OF AMMONIUM PERCHLORATE
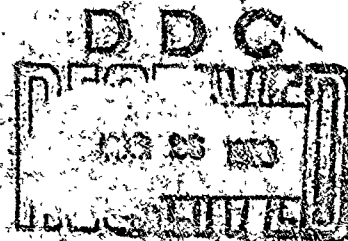
by

G. S. Pearson

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MAY 1969

R O C K E T   P R O P U L S I O N   E S T A B L I S H M E N T

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MECHANISM OF THE DECOMPOSITION OF AMMONIUM PERCHLORATE

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SUMMARY

Although it is generally accepted that the principal initial step in the decomposition of ammonium perchlorate is proton transfer, details of the subsequent reactions have not been resolved. In this Report, full use is made of recently published data on perchloric acid and chlorine dioxide flames, on the oxidation of ammonia, on the reactions of nitroxyl and on the reactions of the chlorine oxides, to deduce a detailed mechanism for the chemical decomposition of ammonium perchlorate. Whilst emphasis has been given to the high temperature decomposition, the basic mechanism is adaptable to a wide range of conditions: to the low temperature decomposition, to combustion, to the catalysed decomposition and to decomposition under various reactive gases. The central feature of the mechanism is that, in the decomposition of ammonium perchlorate, ammonia is oxidized principally by the CIO radical.

<p style="text-align:center">CONTENTS</p>

1   INTRODUCTION

The decomposition of ammonium perchlorate has been studied intensively during the past decade. This particular interest in a single material has arisen because of its use as an oxidizer in solid propellents and has resulted in an immense literature, described in three recent reviews[1,2,3]. Despite the close attention that ammonium perchlorate (AP) has received, many chemical problems concerning its behaviour have remained unsolved. It is the purpose of this Report to consider some of these problems, to suggest solutions, and to survey the existing evidence which might permit a choice to be made between several alternatives.

The general features of the reaction[4,5,6,7] are well known and so these will be described only briefly. The kinetics are usually followed either by weight loss or by pressure measurements. After an induction period the reaction at first accelerates and then decelerates, but the latter stage is not due to the total consumption of reactant as is usual for solid state reactions. Instead a residue of AP remains: on raising the temperature this residue sublimates, but if sublimation is retarded by increasing the ambient pressure then further chemical decomposition occurs.

These three processes, low-temperature decomposition, sublimation, and high-temperature decomposition can be understood in terms of a single mechanism only if the initial process is one of proton transfer[8]

$$NH_4^+ClO_4^-(s) \rightleftharpoons NH_3(a) + HClO_4(a) \tag{1}$$
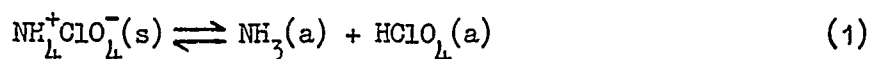
yeilding adsorbed ammonia and perchloric acid. Mutual reaction, at least beginning in the adsorbed phase, helps to sustain the low-temperature reaction; evaporation into the gas phase followed by recombination on a cold surface represents sublimation; decomposition of perchloric acid in the gas phase followed by oxidation of ammonia constitutes the high-temperature reaction. A prominent feature of the decomposition is its susceptibility to catalysis. At high temperatures various metal oxides (notably of the transition metals) are effective catalysts and their activity can be understood[9] if they provide sites for the heterogeneous decomposition of perchloric acid.

The above explanation of the gross features of the reaction are probably acceptable to most workers in the field: unsolved problems, about which much controversy prevails, are (i) the detailed chemical reactions which lead to

the final products, both at low temperatures and at high temperatures; (ii) catalysis of the low-temperature reaction; (iii) the role (if any) of electron-transfer processes; (iv) the chemistry of combustion reactions involving AP. It is these questions to which we address ourselves in this Report, making particular use of recent thermochemical and kinetic evidence.

2   HIGH TEMPERATURE REACTION

The decomposition of perchloric acid above $315^\circ C$ is a first order, homogeneous reaction with a rate constant[10] given by

$$k_2 = 5.8 \times 10^{13} \exp (-45\ 100/RT) \sec^{-1} \quad .$$

The first order kinetics and the magnitude of the activation energy indicate that the rate determining step is

$$HOClO_3 \longrightarrow HO + ClO_3 \qquad\qquad (2)$$

as the bond dissociation energy[11], $D(HO-ClO_3)$, is 47.6 kcal mole^{-1}. The earliest mechanism proposed[6] for the oxidation of NH_3 was that it was brought about by O atoms produced from the decomposition of $HClO_4$; more recent work, however, suggests that the principal oxidizer is likely to be ClO rather than O atoms[12,13]. Thus, although the oxidation of ammonia by O atoms proceeds, as expected, at lower temperatures $(350\text{-}600^\circ K)$ than the reaction of NH_3 with molecular oxygen, and the stoichiometry reported by Wong and Potter[14],

$$NH_3 + 4.4\ O \longrightarrow NO + 0.5\ N_2 + 1.2\ O_2 + 1.0\ H_2O \qquad\qquad (3)$$
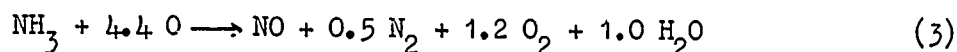
and more recently by Wolfrum[15], in the range 300 to $1000^\circ K$,

$$NH_3 + 2.9\ O \longrightarrow NO + 1.6\ H + 0.6\ O_2 + 0.7\ H_2O \qquad\qquad (4)$$
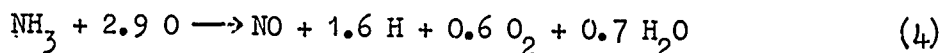
results in formation of nitric oxide, as is observed in the products from AP decomposition, the presence of hydrogen and the absence of nitrous oxide are in marked contrast to the AP product distribution (see Table 1).

It should be emphasised that the AP system is oxidizer-rich and thus the AP product distributions should be compared to other oxidizer-rich mixtures. In studies of ammonia-oxygen flames, nitric oxide has been observed in much smaller

quantities than nitrogen in both oxidizer-rich and stoichiometric mixtures[16,17], with nitrous oxide being observed only as an intermediate[17]. This again contrasts with the products from AP combustion (Table 1) which contain significant amounts of nitrous oxide.

It may therefore be concluded that in the AP system, the oxidation of ammonia proceeds by some species other than oxygen atoms or hydroxyl radicals. (Reaction of ammonia with hydrogen atoms is excluded by the oxidizer-rich nature of the AP system.) This species is considered to be the ClO radical because a mass spectrometric study[18] of the thermal decomposition of perchloric acid has shown that the major products are ClO and ClO_2. Thus reaction (2) must be followed by the rapid reaction

$$ClO_3 \longrightarrow ClO + \underline{O_2} \quad , \quad \Delta H = -12.8 \text{ kcal/mole} \qquad *(5)$$
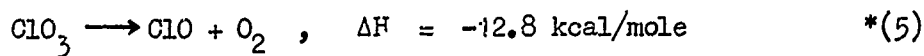
as chlorine trioxide was not observed mass spectrometrically even when ClO_3F, Cl_2O_7 and Cl_2O_6 were pyrolysed[19]. The route by which chlorine dioxide was formed in the pyrolysis of $HClO_4$ at low pressures in the mass spectrometer experiments was considered[18] to be

$$HClO_4 \xrightarrow{\text{surface}} HO_2 + ClO_2 \quad , \quad \Delta H = 31.1 \text{ kcal/mole} \qquad (6)$$
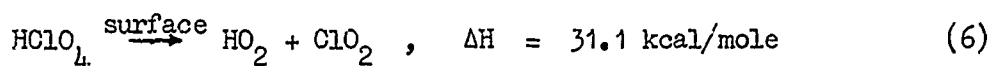
rather than by the fission of a single O atom from ClO_3, a process which is endothermic to the extent of 47.6 kcal/mole. However on catalysts, reaction (2) followed by

$$ClO_3 \longrightarrow ClO_2 + O \quad , \quad \Delta H = 47.6 \text{ kcal/mole} \qquad (6')$$
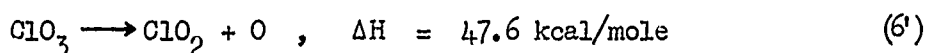
may well be favoured to the extent of becoming the principal route to ClO_2, rather than reaction (6). But ClO_2 molecules, if formed in the AP decomposition, are expected to react rapidly either with O atoms or with Cl atoms (which, along with ClO, are the principal chain carriers in the homogeneous gas phase decomposition of ClO_2) by

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*All enthalpy changes refer to $25°C$ unless otherwise specified. Heats of formation were taken from the JANAF tables. The principal stable products are underlined.

$$O + ClO_2 \longrightarrow ClO + \underline{O_2} \quad , \quad \Delta H = -60.4 \text{ kcal/mole} \qquad (7)$$

and

$$Cl + ClO_2 \longrightarrow ClO + ClO \quad , \quad \Delta H = -5.5 \text{ kcal/mole} \quad . \qquad (8)$$
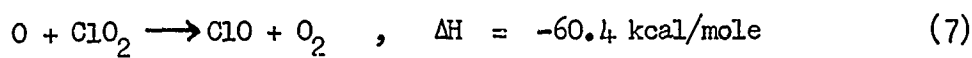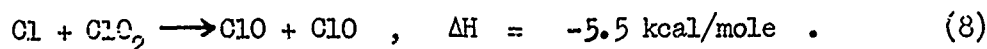
Reactions (7) and (8) have rate constants[20,21] of

$$k_7 > 2 \times 10^{13} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1} \quad , \quad \text{at } 298^\circ K \quad ,$$

and

$$k_8 > 5 \times 10^{11} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1} \quad , \quad \text{at } 298^\circ K \quad ,$$
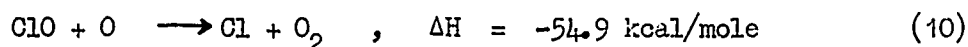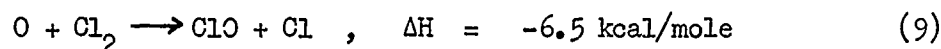
respectively. Thus the end result will be for formation of ClO, although the relative importance of the two possible routes (5), (6') [or (6)] will depend on the conditions, especially of temperature and pressure, and the nature of any catalysts.

The ClO radical is quite stable with a bond dissociation energy[22], $D(Cl-O)$, of 63 kcal mole^{-1}. The rate constant for ClO radical recombination is[23]

$$k_{20} = 7 \times 10^{11} \exp (-2500/RT) \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1} \quad ,$$

which is about five times slower than the chlorine catalysed recombination of O atoms[23]

$$O + Cl_2 \longrightarrow ClO + Cl \quad , \quad \Delta H = -6.5 \text{ kcal/mole} \qquad (9)$$

$$ClO + O \longrightarrow Cl + O_2 \quad , \quad \Delta H = -54.9 \text{ kcal/mole} \qquad (10)$$

with rate constants $k_{10} \gg k_9$ near $300^\circ K$ and

$$k_9 = 5.8 \times 10^{12} \exp (-3100/RT) \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1} \quad .$$

Thus the ClO radical has the necessary stability to be the oxidizer of ammonia and it is formed in high yield by reaction (5), whereas no such mechanism exists for the formation of ClO_2, or of O atoms, in the homogeneous decomposition of $HClO_4$. Even if formed in lower yields by other unsuspected processes, their stability would be lower than that of ClO, as shown above. The lack of O atoms

is further confirmed by the absence of hydrogen and the presence of nitrous oxide in the products, but the statement regarding the absence of ClO_2 may require qualification if there is substantial heterogeneous decomposition of $HClO_4$, as in the presence of oxide catalysts. Early analytical work[4] indicated ClO_2 to be a product of the AP decomposition, but it now appears that ClO_2 is only obtained as a major product from the decomposition of AP containing catalyst or carbon black[24,25], possibly by reaction (6) or (6').

Detailed studies of perchloric acid flames[26] have indicated the presence of a chlorine-oxygen species which is more reactive than oxygen. This is primarily based on (i) the faster burning velocity of perchloric acid flames than of the corresponding flame with oxygen with the same flame temperature and (ii) the production of a second flame zone when oxygen is added to a fuel-rich perchloric acid flame. This conclusion is confirmed by the similar behaviour and nature of fuel-chlorine dioxide flames[27] which also exhibit (i) and (ii). Finally, the products observed[28] in the reaction of H atoms with Cl_2O are O_2 and Cl_2 as major products, and HCl and H_2O as minor products, which is in agreement with Table 1 when allowance is made for the greater H_2O concentration in the AP products.

All this recent evidence points to the principal hydrogen - abstraction reaction involving NH_3 being

$$NH_3 + ClO \longrightarrow NH_2 + ClOH \quad , \quad \Delta H = 5.1 \text{ kcal/mole} \qquad (11)$$

followed by

$$NH_2 + O_2 \longrightarrow HNO + OH \quad , \quad \Delta H = -6.2 \text{ kcal/mole} \quad . \qquad (12)$$

This second step is favoured because the dual role of perchloric acid as an oxidizer, by producing both ClO and molecular oxygen, has been shown in perchloric acid-methane flames[29]. The reaction of NH_2 that is generally accepted in ammonia-oxygen, -nitrous oxide and -nitric oxide flame systems[30] is

$$NH_2 + NO \longrightarrow \underline{N_2} + H + OH \quad , \quad \Delta H = -0.5 \text{ kcal/mole} \qquad (13)$$

but it is less likely than reaction (12) in the AP system because it is improbable that NH_2 radicals will survive long enough to react substantially with

NO which is itself a product of the oxidation of NH_2. The same remark applies a fortiori to the reaction of NH_2 with NO_2, which would be formed at a later stage still by oxidation of NO. Consequently, the reaction of NH_2 radicals with NO_2,
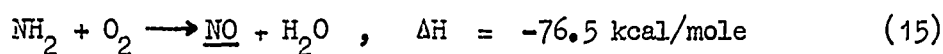
$$NH_2 + NO_2 \longrightarrow \underline{N_2O} + \underline{H_2O} \quad , \quad \Delta H = -10.0 \text{ kcal/mole} \quad (14)$$
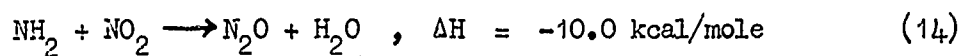
is considered much less likely than the reaction of NH_2 with O_2. Reaction (12) was also proposed in flash photolysis studies[31] of the ammonia - oxygen system when NO and N_2O were observed as major products (cf Table 1).

Other products may be suggested for reaction (12). Thus

$$NH_2 + O_2 \longrightarrow \underline{NO} + \underline{H_2O} \quad , \quad \Delta H = -76.5 \text{ kcal/mole} \quad (15)$$

is thermodynamically favourable, and is equivalent to further reaction between the products of reaction (12). It was concluded from shock-tube studies[32] that reaction (15) would be unlikely to lead to rapid chain propagation (which, however, is not a requirement at this stage of the AP decomposition). Another possibility is

$$NH_2 + O_2 \longrightarrow NH + HO_2 \quad , \quad \Delta H = 43.9 \text{ kcal/mole} \quad (16)$$
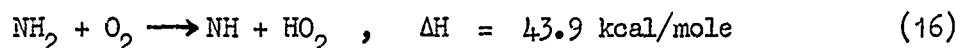
which was proposed from other shock-tube studies[33], but this is unlikely on account of both the endothermic nature of reaction (16) and of recent observations on the NH species in shock tubes[30].

The products in reaction (12) are favoured because they simulate the generally accepted step in hydrocarbon combustion

$$CH_3 + O_2 \longrightarrow CH_2O + OH \quad (17)$$

and also because reaction (12) requires only two bonds to be broken in the transition state whereas reaction (15) requires three bonds to be broken. Thus the relative importance of reactions (12) and (15) will depend critically on the actual geometry of the transition state.

ClO radicals are thus the principal chain carriers, being regenerated by the reactions

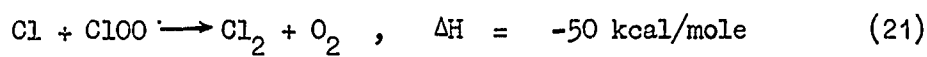$$ClOH + OH \longrightarrow ClO + \underline{H_2O} \quad , \quad \Delta H = -20.9 \text{ kcal/mole} \tag{18}$$

$$ClOH + Cl \longrightarrow ClO + \underline{HCl} \quad , \quad \Delta H = -4.8 \text{ kcal/mole} \ . \tag{19}$$
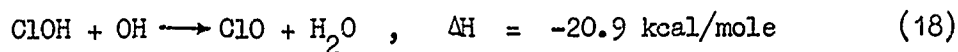
Chain termination proceeds by the reactions[20]

$$ClO + OCl \longrightarrow ClOO + Cl \quad , \quad \Delta H = 1.5 \text{ kcal/mole} \tag{20}$$

$$Cl + ClOO \longrightarrow \underline{Cl_2} + \underline{O_2} \quad , \quad \Delta H = -50 \text{ kcal/mole} \tag{21}$$

$$ClOO + M \longrightarrow Cl + \underline{O_2} + M \quad , \quad \Delta H = 7.9 \text{ kcal/mole} \tag{22}$$

which also provide the Cl atoms required for reaction (19). At high temperatures, the ClOO radical will be short lived and will rapidly decompose by reactions (22) or (21). Likewise, it is improbable that Cl_2O_3, recently reported by McHale and von Elbe[34], will have any but the most transitory existence.

The production of the oxides of nitrogen and especially of N_2O in the products from AP decomposition has long been an unresolved problem. A recent explanation[35] invoked the formation of nitroxyl, HNO, as an intermediate with N_2O resulting from the bimolecular decomposition reaction

$$HNO + HNO \longrightarrow \underline{H_2O} + \underline{N_2O} \quad , \quad \Delta H = -85.8 \text{ kcal/mole} \ . \tag{23}$$
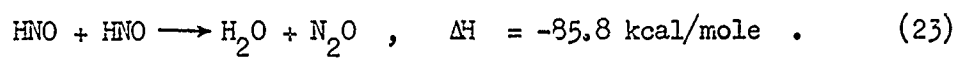
Alternatively, nitroxyl may react with nitric oxide[36]

$$HNO + NO \longrightarrow OH + N_2O \quad , \quad \Delta H = -16.5 \text{ kcal/mole} \ . \tag{24}$$
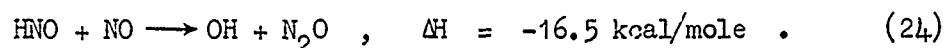
The main difficulty lay in the formation of HNO. This is now overcome by acceptance of reaction (12) in which it is readily produced. There are several reactions involving nitroxyl which may be competitive with reactions (23) and (24). The unimolecular decomposition

$$HNO \longrightarrow H + \underline{NO} \quad , \quad \Delta H = 49.9 \text{ kcal/mole} \tag{25}$$
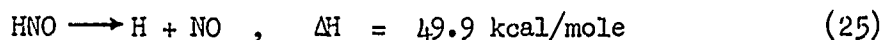
is endothermic but may occur at high temperatures, thus accounting for the decreased yield of N_2O from AP at high temperatures. Two reactions of HNO with oxygen molecules are thermodynamically quite feasible:

$$HNO + O_2 \longrightarrow \underline{NO} + HO_2 \quad , \quad \Delta H \simeq 1 \text{ kcal/mole} \qquad (26)$$

and

$$HNO + O_2 \longrightarrow \underline{NO_2} + OH \quad , \quad \Delta H = -6.6 \text{ kcal/mole} \quad , \qquad (27)$$

as is

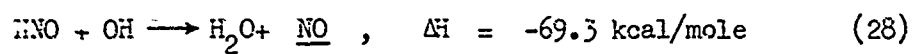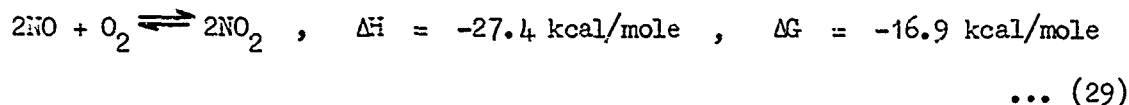$$HNO + OH \longrightarrow \underline{H_2O} + \underline{NO} \quad , \quad \Delta H = -69.3 \text{ kcal/mole} \qquad (28)$$
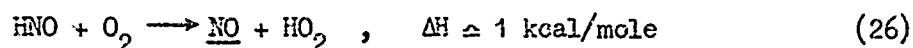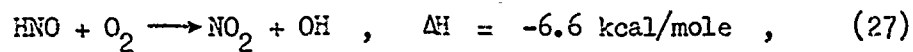
which was proposed[15] to account for the NO production in the $NH_3 + O$ reaction, and has[37] a rate constant

$$k_{28} = 9 \times 10^{13} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$$

between 1600 and 2000°K. Note, however, that reactions (12) + (28) are together equivalent to reaction (15).

NO_2 was not identified in the early analytical work[4,38] but Rosser, Inami and Wise[25] found substantial amounts of HNO_3 through analysis of condensed products. Further, NO_2 was identified as a major product when secondary reactions were reduced by low pressure sampling[24]. Direct oxidation of NO is feasible

$$2NO + O_2 \rightleftharpoons 2NO_2 \quad , \quad \Delta H = -27.4 \text{ kcal/mole} \quad , \quad \Delta G = -16.9 \text{ kcal/mole}$$
$$\cdots (29)$$

but the equilibrium will favour the NO side as the temperature is raised. It is therefore considered that an alternative route must exist and that this must involve a more reactive species than O_2 molecules. The most probable reaction is

$$NO + ClO \longrightarrow \underline{NO_2} + Cl \quad , \quad \Delta H = -9.0 \text{ kcal/mole} \qquad (30)$$
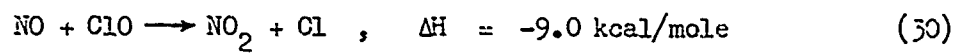
which has been shown[39] along with the reaction

$$NO + OClO \longrightarrow \underline{NO_2} + ClO \quad , \quad \Delta H = -14.5 \text{ kcal/mole} \qquad (31)$$
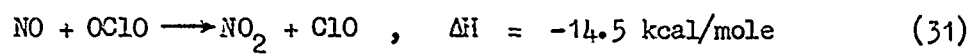
to be fast at $294°K$ since $k_{30}/k_{31} = 0.30$ and

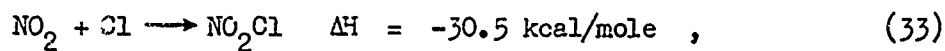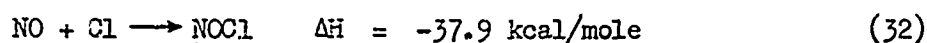$$k_{31} \geq 5 \times 10^{11} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1} .$$

The amount of NO_2 surviving dissociation into NO and O_2 through attempted establishment of the equilibrium (29) will then depend on the temperature and the residence time of NO_2 molecules in the hot zone. The rate constant for the back reaction in reaction (29) has been considered by Schofield[40] who fitted all the data points to

$$k_{-29} = 2.1 \times 10^{13} \exp (-28\ 360/RT) \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1} .$$

The small amount of N_2 found in the AP products, much less than N_2O at low temperatures, will be formed by reaction (13). The relative importance of the four suggested main routes for the oxidation of NH_2, namely reactions (12) + (28) [or (15)], which produce NO; reactions (12) + (23), which produce N_2O; reaction (13), which produces N_2 with consumption of NO; and reactions (12) + (24) which produce N_2O with consumption of NO, will control the relative amounts of N_2, N_2O and NO and this fact provides an explanation for the observed temperature-dependence of the N-containing products from AP.

The above reaction scheme provides a rational explanation of the appearance of the principal products H_2O, O_2, Cl_2, HCl, N_2 NO and NO_2. $NOCl$ and NO_2Cl are also formed in trace amounts and clearly result from secondary processes

$$NO + Cl \longrightarrow \underline{NOCl} \quad \Delta H = -37.9 \text{ kcal/mole} \tag{32}$$

$$NO_2 + Cl \longrightarrow \underline{NO_2Cl} \quad \Delta H = -30.5 \text{ kcal/mole} , \tag{33}$$

whilst HNO_3 will most likely be formed at the wet chemical stage: this will have to be reconsidered if HNO_3 can be detected in the gas phase close to the decomposing AP.

A newly constructed table of product analyses is given as Table 1. In addition to representative analyses obtained from static methods[4,38] this includes results from a flow method[41] and from mass spectrometric analyses. Pellett and Saunders[24] have expressed their results as ratios of mole product to moles HCl. These have been converted to the molar ratios in Table 1 assuming a

hydrogen balance. Thus the relative values will be correct but the absolute values may be somewhat in error if there are other H-containing products besides HCl and H_2O in the mass spectrometer (high vacuum) experiment. It seems unlikely that the tabled values are subject to large errors, because an H-balance ($H_2O + HCl + HNO_3$) on the data of Rosser, Inami and Wise[41] yields 1.84 mole H_2O per mole of AP (<300°C) whereas an H-balance assumption on Pellett and Saunders' data ($H_2O + HCl$) yields 1.78 mole H_2O at 280°C and 1.84 mole H_2O at 180°C, per mole of AP. Thus the data from the two techniques are directly comparable.

The most obvious difference is the large amount of NO_2 found on low-pressure sampling and this is evidence for a reaction that leads to NO_2 directly without the need for establishing the $NO + O_2$ equilibrium. The decreased yield in NO_2 as the temperature increases is simply due to the decreasing stability of NO_2. The large yield of HCl, at the expense of Cl_2, and its substantial increase with temperature seem to be special features of the mass spectrometric method. The reasons are not apparent to us (cf Ref.18), except that HCl is thermally more stable than Cl_2. [$D(H-Cl) = 103.1$ kcal/mole and $D(Cl-Cl) = 57.8$ kcal/mole.]

3   LOW TEMPERATURE REACTION

No sharp boundary exists between the low-temperature and high-temperature reactions. Nevertheless the experimental fact exists that AP leaves a residue which decomposes only slowly below about 270°C. Differentiation between the two reactions in terms of products is less useful than once appeared[42] as there is a gradual reduction in the yield of N_2O as the temperature is increased and this effect begins well below temperatures usually associated with the high-temperature reaction. Correlation of product yields with fractional decomposition might be a useful exercise, but the data for a thorough analysis do not exist. More significant criteria are the different kinetics, the sensitivity of the rate constant for the high-temperature reaction to ambient pressure and reactant mass (when k is deduced by weight loss[43]) and the different activation energies deduced from weight-loss and pressure measurements[8]. These suggest that at high temperature gas phase reactions are rate determining, and the solid phase process is a simple evaporation of NH_3 and $HClO_4$, as assumed above. In contrast, for the kinetics of the low-temperature reaction, weight loss and pressure increase methods yield essentially the same rate constant and activation energy[35].

The continuous nature of the changes in product distribution (there are really few data for the high-temperature reaction > $300^{\circ}C$) and the similarity in the activation energy for the low-temperature reaction and that for sublimation, point to the rate-determining step in both cases being proton transfer on the surface (presumably at 'steps'). The insensitivity of the low-temperature reaction to ambient pressure and its cessation by NH_3 poisoning[35] point to a surface reaction on the perchlorate itself. There are two possibilities: direct reaction of NH_3 with $HClO_4$ and heterogeneous decomposition of $HClO_4$. Two experiments[11,44,45] point to the reaction of NH_3 with $HClO_4$ in the gas phase as a vigorous one under certain conditions, but at low temperatures, on a substrate, the reversal of proton transfer is the more likely result, as shown[35] by the poisoning of the reaction by excess NH_3. This leaves the heterogeneous decomposition of $HClO_4$ as the key step. Once this occurs the rest of the mechanism will be essentially that outlined above for the high-temperature reaction.

One of the outstanding features of the low-temperature reaction that has never been properly explained is its catalysis by a wide range of cations and anions. Because $HClO_3$ is a weaker acid than $HClO_4$, ClO_3^- ions will be better proton acceptors than ClO_4^- ions. ClO_3^- ions may therefore function as nuclei-forming sites and this may explain the pronounced effects of pre-irradiation with X-rays which are known to form ClO_3 radicals[46,47] and therefore presumably ClO_3^- ions. It is known, for example, that NH_4ClO_3 is much less stable than NH_4ClO_4, evidence in favour of the easier proton transfer to ClO_3^-. Cation catalysis, by Ag^+ for example[48], does not find a ready explanation in terms of this mechanism except by the formation of ammine complexes[49] which will reduce the probability of the reverse of reaction (1) in which NH_3 molecules are acting as proton acceptors.

4   COMBUSTION

The really striking feature of the product analyses from the combustion zone of AP is the similarity to those from low temperature decomposition. Most of the existing combustion data relate to pressures well above 1 atm or to the catalysed reaction. Some representative 1 atm data for the combustion of pure AP assisted by pre-heating, radiation, or external heating are shown in Table 1. The figure shown jointly for NO, NO_2 and HNO_3 includes also NOCl and NO_2Cl which are presumed to be formed by secondary processes, reactions (32) and (33). The similarity in the products from thermal decomposition and from combustion
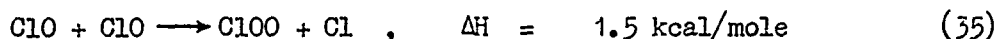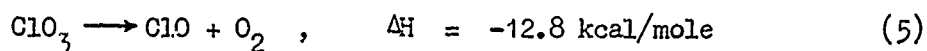
implies a similarity in mechanism and we suggest, therefore, that the combustion process comprises, as its main features:
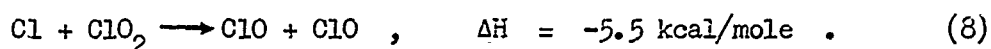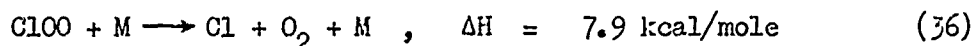
(i)   proton transfer from NH_4^+ to ClO_4^-;

(ii)   evaporation of NH_3 and $HClO_4$;

(iii)   decomposition of $HClO_4$ yielding ClO;

(iv)   radical attack on HN_3 by ClO to give NH_2;

(v)   oxidation of NH_2 by O_2 to give HNO and NO;

(vi)   oxidation of NO by ClO to give NO_2;

(vii)   reaction of HNO with HNO or NO to give N_2O;

(viii) reaction of NO with NH_2 to give N_2;

(ix)   reaction of Cl with ClOH to give HCl.

It should be noted that all the gas phase reaction steps (iv) - (ix) with the exception of (vii) involve radicals, and are therefore presumed to be kinetically fast.

5   CATALYSED REACTION

It has been proposed[9] that oxide catalysts act kinetically by facilitating the decomposition of $HClO_4$ heterogeneously. A mass spectrometric technique[24] has shown that AP, mixed with copper chromite or carbon black, decomposes under laser action to yield a high quantity of ClO_2. Thus, following (1), reaction (6') replaces the usual homogeneous reaction (5), or possibly, as suggested by Fisher[18], reaction (6) is substituted for reaction (2). At normal pressures ClO_2 decomposes by a chain process; at low temperatures this involves Cl_2O_3 (Ref.34) but at the temperature of the AP decomposition the formation of Cl_2O_3 is unlikely because the equilibrium will favour $ClO + ClO_2$. Thus the ClO_2 decomposition will involve

$$ClO_2 + ClO_2 \longrightarrow ClO + ClO_3 \quad , \quad \Delta H = \quad 11.2 \text{ kcal/mole} \tag{34}$$

$$ClO_3 \longrightarrow ClO + O_2 \quad , \quad \Delta H = \quad -12.8 \text{ kcal/mole} \tag{5}$$

$$ClO + ClO \longrightarrow ClOO + Cl \quad , \quad \Delta H = \quad 1.5 \text{ kcal/mole} \tag{35}$$

$$ClOO + M \longrightarrow Cl + O_2 + M \quad , \quad \Delta H = 7.9 \text{ kcal/mole} \tag{36}$$

$$Cl + ClOO \longrightarrow Cl_2 + O_2 \quad , \quad \Delta H = -50 \text{ kcal/mole} \tag{37}$$

$$Cl + ClO_2 \longrightarrow ClO + ClO \quad , \quad \Delta H = -5.5 \text{ kcal/mole} \quad . \tag{8}$$

Apart from the three-bodied combination of Cl atoms, and the reaction of ClOO with Cl, which terminate the chains, the overall result is

$$ClO_2 \longrightarrow ClO + \tfrac{1}{2} O_2 \quad , \quad \Delta H \simeq -1 \text{ kcal/mole} \quad . \tag{38}$$
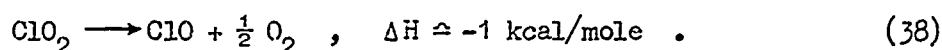
The remainder of the mechanism, as discussed above for the uncatalysed high-temperature decomposition of AP, may, with one important difference, hold for the catalysed reaction. This difference arises because (a) ·Cl atoms are formed earlier in the reaction sequence, permitting reaction (19) to take place earlier, and (b) the formation of ClO requires decomposition of the ClO_2 intermediate. Thus, there is a greater chance of ClO and NH_2 existing together than in the homogeneous reaction. Consequently, in addition to the oxidation of NH_2 by O_2, the reaction

$$NH_2 + ClO \longrightarrow HNO + \underline{HCl} \quad , \quad \Delta H = -62.8 \text{ kcal/mole} \tag{39}$$
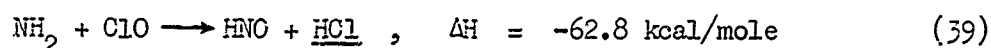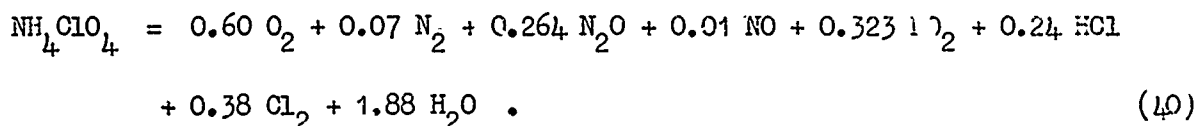
has to be considered. By analogy with the reaction postulated to account for the cool-flame bands observed in $CH_4 + HClO_4$ flames, one would expect HNO to be in an excited state and thus to decompose rapidly to H + NO. Consequently the yield of N_2O will be decreased and that of NO increased proportionately. There is little definitive information on product changes caused by the presence of catalysts but MnO_2, Co_2O_3, NiO, Fe_2O_3 and Cr_2O_3 all reduce the yield of N_2O with a corresponding increase in the yield of NO.

6 STOICHIOMETRY

There is no such thing as a chemical equation which describes uniquely the decomposition of AP because the nature and relative proportions of the products depend on the conditions (especially temperature, pressure, and the presence of catalysts) as well as on the sampling technique employed. Nevertheless there is much agreement about the principal products (Table 1; see Refs.2 and 3 for greater detail) and the following equation may be regarded as

a typical average representation of the stoichiometry of the AP decomposition:

$$NH_4ClO_4 = 0.60\ O_2 + 0.07\ N_2 + 0.264\ N_2O + 0.01\ NO + 0.323\ N_2 + 0.24\ HCl$$
$$+ 0.38\ Cl_2 + 1.88\ H_2O\ . \tag{40}$$

The principal reactions contributing to the mechanism are summarized in Table 1, together with multiplying factors which give the stoichiometry (40). The main doubt concerns the bimolecular decomposition of HNO, reaction (i). In scheme A, we have assumed that the N_2O comes from the reaction of HNO + NO, reaction (j). No unique solution is then possible, because (f) + (q) is equivalent to (g). Thus the overall stoichiometry is satisfied by any combination of x and y satisfying the relation x + y = 0.667. In scheme B we have made the converse assumption that the N_2O comes from (i), rather than (j). The resulting factors are shown in Table 2.

It is interesting to see what changes in the mechanism are required at combustion temperatures. Scheme C is based on the same assumptions as B and gives the stoichiometric factors necessary to fit the products from AP combustion, as determined by Arden, Powling and Smith[50]. It will be observed as the principal result of the rise in temperature, that HNO decomposes unimolecularly (f), rather than bimolecularly (i), which is to be expected in view of the endothermicity of reaction (25). There is always a doubt as to how much of the NO_2, observed in combustion experiments, arises from secondary oxidation of NO as the products cool. These are reported together in Table 1. In making the calculations for scheme C we have assumed that the primary product is entirely NO, but this assumption does not affect the above conclusion regarding HNO.

Thus we believe that we have arrived at a basic mechanism, kinetically and thermodynamically realistic, which conforms to the observed stoichiometry. Clearly numerous variations are possible by slight changes in the above mole numbers and by adding more reactions to account for special circumstances, such as catalysis.

In such an oxidizer-rich system as AP an important criterion of the validity of any mechanism is that unstable reducing species should not survive for any length of time. Consequently, we have shown the approximate sequence

of the chemical reactions in our mechanism in Fig. 1. The various adjacent regions will overlap, but in no case has an unstable species been postulated to survive for an excessive time.

Appendix A

THE EFFECT OF THE GASEOUS ENVIRONMENT ON THE DECOMPOSITION OF
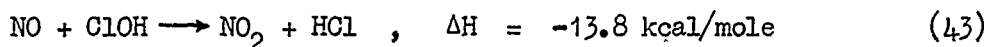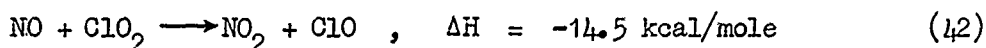## AMMONIUM PERCHLORATE

A.1 Addition of oxygen

Little direct effect is predicted because reaction (12) already has one mole of oxygen available per mole of NH_2. Secondary effects might arise if

$$HNO + O_2 \longrightarrow NO + HO_2 \qquad\qquad \cdot (26)$$

$$HNO + O_2 \longrightarrow NO_2 + OH \qquad\qquad (27)$$

are fast enough to be competitive with reaction (23). Thus the yield of N_2O would decrease.

A.2 Addition of nitric oxide

This is a reactive substance and there are consequently several possibilities. First, it can react with ClO_2 and $ClOH$ according to

$$NO + ClO_2 \longrightarrow NO_2 + ClO \quad , \quad \Delta H = -14.5 \text{ kcal/mole} \qquad (42)$$

$$NO + ClOH \longrightarrow NO_2 + HCl \quad , \quad \Delta H = -13.8 \text{ kcal/mole} \qquad (43)$$

thus increasing the NO_2 and HCl yields and providing an extra source of ClO. At low NO concentrations, this will react principally with NH_3* according to reaction (11), which yields NH_2 and ClOH, the latter being consumed by reaction (43). The increased production of NH_2 radicals means greater consumption of O_2, according to reaction (12) and the corresponding increase in HNO will result in an increased yield of N_2O. Thus on the basis of the proposed mechanism, one predicts that the effect of adding nitric oxide will be:

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*It must be recalled that although NH_3 is not a stable product at ordinary pressures, under the high-vacuum conditions prevailing in a mass spectrometric study NH_3, and also NH_2Cl (from $NH_3 + Cl_2$), are observed. Similarly ClO_2 is commonly found in mass spectrometric investigations.

(i)   decreased yields of NH_3, O_2, ClO_2, ClOH;

(ii)   increased yields of HCl, NO_2 and N_2O.

These are substantially the results of Majer and Smith[51] for small additions of NO. At higher NO concentrations reaction (30) will result in a reduced concentration of ClO and consequently reaction (11) becomes less important so that the partial pressures of NH_3 and of O_2 (because of a reduction in reaction (12)) increase again. The reduction in HNO (formed in reaction (12)) means a corresponding reduction in N_2O. The initial changes (i) and (ii) will therefore be superseded at high NO concentrations by increases in NH_3 and O_2 and a decrease in N_2O. Because ClO is being removed by reaction with NO, and there is correspondingly less reaction of ClO with NH_3, ClOH is not being produced to the same extent and the HCl yield therefore falls also (see reaction (19)).

A.3   Addition of ammonia

Ammonia retards the proton transfer reaction (1) and therefore the addition of NH_3 reduces all products, except that NH_2Cl will increase by reaction of the added NH_3 with Cl_2.

A.4   Addition of chlorine and hydrogen chloride

Chlorine and hydrogen chloride will both react with NH_3 and thus facilitate reaction (1). Thus Schmidt[52] found that HCl accelerated the decomposition of the first 30% AP whilst Cl_2, in addition, caused complete decomposition at low temperatures. It would be expected that removal of NH_3 would reduce the significance of reactions (11), (12), (15) and (23), with consequent reduction of the yield of oxides of nitrogen. Because ClO reacts to a lesser extent with NH_3 it must be removed by other routes, i.e. through bimolecular combination to yield Cl_2 and O_2. Thus Cl_2, O_2 should increase at the expense of oxides of nitrogen and HCl. Detailed information on these points is, however, not available.

<div align="center">

Table 1

PRODUCTS FROM THE DECOMPOSITION AND COMBUSTION OF AMMONIUM PERCHLORATE
EXPRESSED AS MOLES PER MOLE OF AP DECOMPOSED

</div>

Authors	Ref.	O_2	N_2	N_2O	NO	NO_2	HNO_3	HCl	Cl_2	Temp.°C
Decomposition										
Bircumshaw	4.	0.51	0.13	0.36	-			0.16*	0.43	225
& Newman		0.57	0.06	0.44	0.015			0.14*	0.39	275
Shmagin et al.	38	0.75	0.05	0.29	0.32			0.22	0.39	280
Rosser, Inami and Wise	41	0.52	0.05	0.36	0.015		0.17	0.16	0.39	275
Pellett and	24	0.69		0.35		0.42		0.32	0.38	180
Saunders		0.62		0.27		0.20		0.44	0.23	280
		0.42		0.21		0.17		0.52	0.15	380
Combustion										
Levy and Friedman	53	0.65	0.11	0.10		0.55			0.50	**
Arden, Powling and Smith	50	0.68	0.07	0.11		0.69		0.25	0.39	970⟋
Kuratani	54	0.75	0.19	0.12		0.38			0.31	⟋⟋

*   Recorded as 'total acid'.

**   Combustion at atmospheric pressure with the aid of radiation.

⟋   Flame temperature; AP was pre-heated to 280°C.

⟋⟋   With external heating until ignition.

Table 2

STOICHIOMETRY FOR THE DECOMPOSITION OF AMMONIUM PERCHLORATE

	Reaction	Multiplying factors			Eq. No. in text
		A	B	C	
(a)	$NH_4ClO_4 \longrightarrow NH_3 + HClO_4$	1	1	1	(1)
(b)	$HClO_4 \longrightarrow ClO + \underline{O_2} + OH$	1	1	1	(2) + (5)
(c)	$ClO + NH_3 \longrightarrow NH_2 + ClOH$	1	1	1	(11)
(d)	$ClOH + OH \longrightarrow \underline{H_2O} + ClO$	0.76	0.76	0.76	(18)
(e)	$NH_2 + O_2 \longrightarrow HNO + OH$	0.93	0.93	0.93	(12)
(f)	$HNO \longrightarrow H + \underline{NO}$	x	0.403	0.74	(25)
(g)	$HNO + OH \longrightarrow \underline{NO} + \underline{H_2O}$	y	0	0	(28)
(h)	$NH_2 + NO \longrightarrow \underline{N_2} + H + OH$	0.07	0.07	0.07	(13)
(i)	$HNO + HNO \longrightarrow \underline{N_2O} + \underline{H_2O}$	0	0.264	0.095	(23)
(j)	$HNO + NO \longrightarrow \underline{N_2O} + OH$	0.264	0	0	(24)
(k)	$ClO + ClO \longrightarrow 2Cl + \underline{O_2}$	0.339	0.338	0.50	(35) + (36)
(l)	$ClOH + Cl \longrightarrow ClO + \underline{HCl}$	0.24	0.24	0.25	(19)
(m)	$NO + ClO \longrightarrow \underline{NO_2} + Cl$	0.323	0.323	0	(30)
(n)	$Cl + Cl + M \longrightarrow \underline{Cl_2} + M$	0.38	0.38	0.375	(41)
(p)	$OH + OH \longrightarrow \underline{H_2O} + \frac{1}{2}O_2$	0.383	0.383	0.22	(42)
(q)	$H + OH \longrightarrow \underline{H_2O}$	x + 0.07	0.473	0.84	(43)

$$x + y = 0.667$$

REFERENCES

No.	Author	Title, etc.
1	C. U. Pittman	U.S. Army Missile Command, Redstone Arsenal, RK-TR-66-13, August 1966
2	A. R. Hall G. S. Pearson	Mintech R.P.E. Technical Report 67/1 (1967); Combustion Reviews, ed. C. F. H. Tipper, Vol.III, No.2, pp.199-239, Amsterdam, Elsevier (1968)
3	P. W. M. Jacobs H. M. Whitehead	Chem. Rev., in press
4	L. L. Bircumshaw B. H. Newman	Proc. Roy. Soc. (London), $\underline{A227}$, 115-132 (1954)
5	L. L. Bircumshaw B. H. Newman	Ibid, $\underline{A227}$, 228-241 (1955)
6	A. K. Galwey P. W. M. Jacobs	J. Chem. Soc., 837-844 (1959)
7	A. K. Galwey P. W. M. Jacobs	Proc. Roy. Soc. (London), $\underline{A254}$, 455-469 (1960)
8	P. W. M. Jacobs A. Russell-Jones	A.I.A.A. Journal, $\underline{5}$, 829-830 (1967)
9	P. W. M. Jacobs A. Russell-Jones	Eleventh Symposium (International) Combustion; pp.457-462, Pittsburgh, The Combustion Institute (1967)
10	J. B. Levy	J. Phys. Chem., $\underline{66}$, 1092-1097 (1962); Atlantic Research Corp. Alexandria, Va., AFOSR Technical Note 1555 (1961) [AD 265 041]
11	G. S. Pearson	Advances in Inorganic and Radiochemistry, $\underline{8}$, 177-224 (1966)
12	G. S. Pearson	Nature (London), $\underline{208}$, 283 (1965)
13	G. S. Pearson D. Sutton	A.I.A.A. Journal, $\underline{5}$, 2101-2103 (1967)
14	E. L. Wong A. E. Potter	J. Chem. Phys., $\underline{39}$, 2211-2217 (1963); Ibid., $\underline{43}$, 3371-3382 (1965)

REFERENCES (Contd.)

No.	Author	Title, etc.
15	E. A. Albers et al.	Twelfth Symposium (International) Combustion, Poitiers, 1968, in press
	J. Wolfrum	Doctoral Thesis, Göttingen (1968)
16	D. G. R. Andrews P. Gray	Combustion and Flame, 8, 113-126 (1964)
17	D. I. McLean H. Gg. Wagner	Eleventh Symposium (International) Combustion, pp.871-878, Pittsburgh, The Combustion Institute (1967)
18	I. P. Fisher	Trans. Faraday Soc., 63, 684-692 (1967); Mintech R.P.E. Technical Report 66/13 (1966)
19	I. P. Fisher	Trans. Faraday Soc., 64, 1852-1857 (1968); Mintech R.P.E. Technical Report 67/10 (1967)
20	M. A. A. Clyne J. A. Coxon	Trans. Faraday Soc., 62, 1175-1189 (1966)
21	M. A. A. Clyne J. A. Coxon	Proc. Roy. Soc. (London), A303, 207-231 (1968)
22	R. A. Durie D. A. Ramsey	Can. J. Physics, 36, 35-53 (1958)
23	M. A. A. Clyne J. A. Coxon	Trans. Faraday Soc., 62, 2175-2182 (1966)
24	G. L. Pellett A. R. Saunders	A.I.A.A. Preprint 68-149 (1968)
25	W. A. Rosser S. H. Inami H. Wise	Combustion and Flame, 12, 427-435 (1968); A.I.A.A. Journal, 4, 1615-1622 (1966)
26	e.g. C. A. McD. Cummings A. R. Hall, also G. S. Pearson	Tenth Symp. (International) Combustion, pp.1365-1372 Pittsburgh, The Combustion Institute (1965) Combustion and Flame, 12, 54-62 (1968)
27	J. Combourieu R. Moreau	Twelfth Symposium (International) Combustion, Poitiers, 1968, in press

REFERENCES (Contd.)

No.	Author	Title, etc.
28	C. G. Freeman L. F. Phillips	J. Phys. Chem., 72, 3031-3032 (1968)
29	A. R. Hall G. S. Pearson	Twelfth Symposium (International) Combustion, Poitiers, 1968, in press
30	P. Gray R. Mackinven D. B. Smith	Combustion and Flame, 11, 109-119 (1967)
31	D. Husain R. G. W. Norrish	Proc. Roy. Soc. (London), A273, 145-164 (1963)
32	J. N. Bradley R. N. Butlin D. Lewis	Trans. Faraday Soc., 64, 71-78 (1968)
33	L. J. Drummond S. W. Hiscock	Australian J. Chem., 20, 825-836 (1967)
34	E. T. McHale G. von Elbe	J. Amer. Chem. Soc., 89, 2795-2797 (1967); J. Phys. Chem., 72, 1849-1856 (1968)
35	J. V. Davies P. W. M. Jacobs A. Russell-Jones	Trans. Faraday Soc., 63, 1737-1748 (1967)
36	M. A. A. Clyne	Tenth Symp. (International) Combustion, pp. 311-316 Pittsburgh, The Combustion Institute (1965)
37	E. M. Bulewics T. M. Sugden	Proc. Roy. Soc. (London), A277, 143-154 (1964)
38	L. F. Shmagin A. A. Shidlovskii	Issled. v Obl. Khim. i Tekhnol. Mineral'n. Solei i Okislov, pp. 112-144, Akad. Nauk SSSR, Sb. Statei (1965); Mintech R.P.E. Translation 18 (1967)
39	J. A. Coxon	Trans. Faraday Soc., 64, 2118-2123 (1968)
40	K. Schofield	Planet. Space Sci., 15, 643-670 (1967)

REFERENCES (Contd.)

No.	Author	Title, etc.
41	W. A. Rosser S. H. Inami H. Wise	Third ICRPG Combustion Conference, John F. Kennedy Space Center, Feb. 1967, CPIA Publication 138, Vol.1, pp.27-28; see also idem, Stanford Research Institute PU 3573, Nonr-3415(00), Sept. 1966 [AD 640 084]
42	M. Dodé	Bull. Soc. Chem. France [5], 5, 170-176 (1938), C.R. Acad. Sci. Paris, 200, 63-66 (1934)
43	P. W. M. Jacobs A. Russell-Jones	J. Phys. Chem., 72, 202-207 (1968)
44	R. Friedman J. B. Levy also J. B. Levy	Atlantic Research Corp., Alexandria, Va. Final Technical Report AFOSR 2005, Dec. 1961 Tenth Symp. (International) Combustion, p.1371 Pittsburgh, The Combustion Institute (1965)
45	F. J. Cheselke	Aerojet-General Corp., Sacramento, Cal., Report 0372-01F, Feb. 1965 [STAR N65-20871; AD 458-854]
46	T. Cole	J. Chem. Phys., 35, 1169-1173 (1961)
47	J. S. Hyde E. S. Freeman	J. Phys. Chem., 65, 1636-1637 (1961)
48	F. Solymosi K. Dobo	Fifth International Symposium on the Reactivity of Solids, Amsterdam, Elsevier (1965); see also Magy. Kem. Folyoirat 72, 124-129 (1966)
49	L. Dauerman	A.I.A.A. Journal, 5, 192 (1967)
50	E. A. Arden J. Powling W. A. W. Smith	Combustion and Flame, 6, 21-33 (1962)
51	J. R. Majer M. Smith	Private communication to G. S. Pearson
52	W. G. Schmidt	Aerojet-General Corp., Sacramento, Cal., Report NASA CR-66457, Sept. 1968

REFERENCES (Contd.)

No.	Author	Title, etc.
53	J. B. Levy R. Friedman	Eighth Symp. (International) Combustion, pp.663-672 Baltimore, Williams &·Wilkins (1962)
54	K. Kuratani	Aeronautical Research Institute, University of Tokyo, Report 374, $\underline{28}$, 115-127 (1962)

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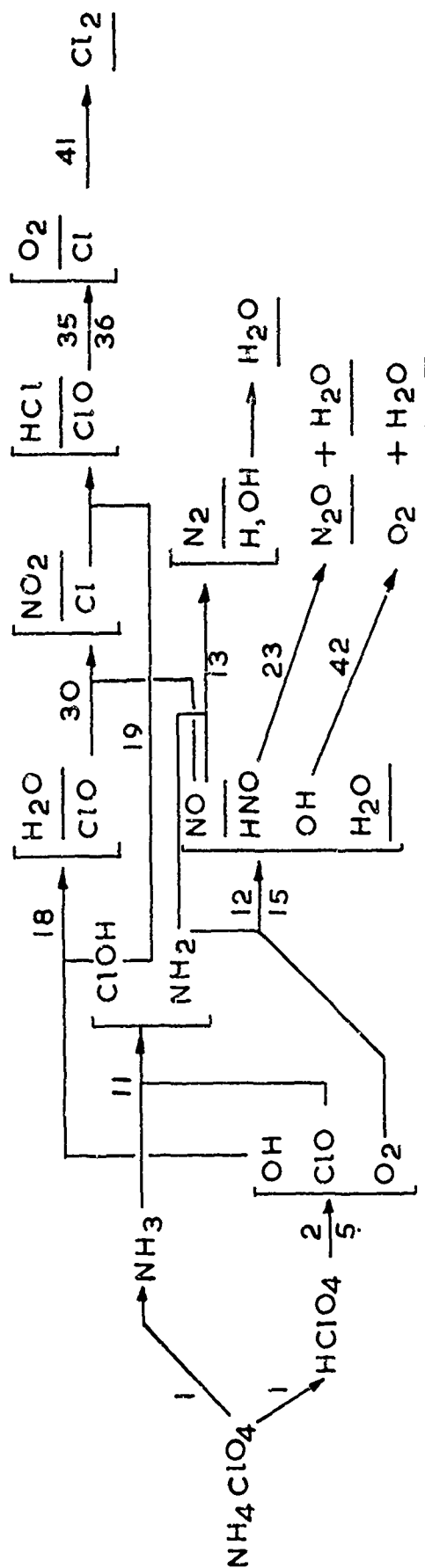
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FIG. 1. SCHEMATIC REPRESENTATION OF THE SEQUENCE OF CHEMICAL REACTIONS IN
THE MECHANISM OF THE DECOMPOSITION OF AMMONIUM PERCHLORATE